



DECLARATION

I, Shigeaki Nishikawa of Nishikawa & Associates, Visual City, Suite 401, 43-9, Higashi-Nippori 3-chome, Arakawa-ku, Tokyo, Japan, do solemnly and sincerely declare that I am well acquainted with both the Japanese language and the English language and that the attached English translation of an officially certified copy of Patent Application No. 2002-260850 is a true and correct translation to the best of my knowledge and belief from the Japanese language to the English language.

Dated this 15th day of November, 2007

Shigeaki Nishikawa

Shigeaki Nishikawa

(translator)

(Translation)

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of
the following application as filed with this Office.

Date of Application: September 6, 2002

Application Number: Patent Application No. 2002-260850

Applicant(s): ZEON CORPORATION

Dated: September 18, 2003

Yasuo Imai
Commissioner, Patent Office

Certificate No. 2003-3076673

[Document Name] Application for Patent

[Docket Number] 2002-134

[To] Hon. Director General of Patent
Office

[International Patent Classification] G03G 9/08
G03G 9/09

[Inventor]

[Address or Domicile] c/o Zeon Corporation, 6-1,
Marunouchi 2-chome, Chiyoda-ku, Tokyo

[Name] Fuminari Oyama

[Inventor]

[Address or Domicile] c/o Zeon Corporation, 6-1,
Marunouchi 2-chome, Chiyoda-ku, Tokyo

[Name] Kazu Niwa

[Applicant for Patent]

[Identification Number] 000229117

[Name] ZEON CORPORATION

[Representative] Katsuhiko Nakano

[Indication of Fee]

[Deposit Account Number] 033684

[Fee] ¥21,000

[List of Materials Submitted]

[Material Name] Specification 1

[Material Name] Abstract 1

[Document Name] Specification

[Title of the Invention] MAGENTA TONER

[Claims]

5 **[Claim 1]** A magenta toner having a magenta toner
particles comprising a binder resin and a magenta pigment,
wherein the magenta pigment is composed of C.I. Pigment Red
31 and C.I. Pigment Red 150.

10 **[Claim 2]** The magenta toner according to claim 1,
wherein the magenta toner particles further comprises a
charge control resin.

15 **[Claim 3]** The magenta toner according to claim 1 or 2,
wherein the magenta pigment contains C.I. Pigment Red 31
and C.I. Pigment Red 150 within the range from 30:70 to
80:20 in terms of a mass ratio.

20 **[Claim 4]** The magenta toner according to any one of
claims 1 to 3, wherein the magenta toner particles has a
core-shell structure.

[Detailed Description of the Invention]

[0001]

25 **[Technical Field to which the Invention Belongs]**

The present invention relates to a magenta toner for
developing an electrostatic latent image formed by an
electrophotographic process, electrostatic recording
process and the like.

30 **[0002]**

[Prior Art]

In an image forming apparatus such as an

electrophotographic apparatus or electrostatic recording apparatus, an electrostatic latent image formed on a photosensitive member is first developed with a toner. After the toner image formed is then transferred to a 5 transfer medium such as paper as needed, the image is fixed thereto by any of various methods such as heating, pressing and use of solvent vapor.

As such image forming apparatus, a digital full-color copying machine and a digital full-color printer are put to 10 practical use. In the digital full-color copying machine, after a colored image original is subjected to color separation through respective filters of blue, green and red, electrostatic latent images composed of a dot diameter of 20 to 70 μm corresponding to the colored image original 15 are developed with respective toners of yellow, magenta, cyan and black colors to form a full-color image making good use of a subtractive mixture effect.

In recent years, a demand for formation of full-color images with high image quality and high definition has more 20 and more increased. In order to improve color reproducibility in particular, it is desirable that an image using color toners can be printed with a hue equivalent to printing with inks. As colorants for magenta toner, have heretofore been positively used organic 25 pigments such as quinacridone pigments, perillene pigments, thioindigo pigments and β -oxynaphthenic anilide pigments (i.e., Naphthol AS pigments). Among these, the

quinacridone pigments are widely used in that they are excellent in light resistance, heat resistance and transparency. With respect to the quinacridone pigments, it has been investigated to use a quinacridone pigment and 5 another quinacridone pigment in combination or use a quinacridone pigment and another magenta pigment in combination for the purpose of improving toner properties.

[0003]

Japanese Patent Application Laid-Open No. 10-312088 10 has proposed a magenta toner making combined use of C.I. Pigment Red 122 and C.I. Pigment Red 57:1. Japanese Patent Application Laid-Open No. 2000-181144 has proposed a magenta toner making combined use of C.I. Pigment Red 122 and at least one red pigment having negatively charging 15 ability or weakly positively charging ability. Japanese Patent Application Laid-Open No. 2002-91086 has proposed a magenta toner making combined use of a quinacridone pigment and a Naphthol AS pigment or β -naphthol lake pigment. However, these toners has involved a problem that toner 20 particles are easy to be broken by contact between the magenta toner particles or stress between a feed roll and a development roll, or between a development and a photosensitive member in an image forming apparatus. When the toner particles are broken, the flowability and 25 printing density of the magenta toner are lowered. In addition, C.I. Pigment Red 57:1 that is used in respective Examples in Japanese Patent Application Laid-Open No. 10-

312088 and Japanese Patent Application Laid-Open No. 2002-91086 is poor in light resistance, and so the resulting image may be faded. Further, since C.I. Pigment Red 5 and C.I. Pigment Red 209 that are used in respective Examples 5 in Japanese Patent Application Laid-Open Nos. 2000-181144 and 2002-91086 are chlorine atom-containing compounds, there is a possibility that dioxin may be generated when paper, on which images have been formed, is incinerated and may cause environmental problems.

10 Japanese Patent Application Laid-Open No. 2000-156795 discloses magenta toners containing C.I. Pigment Red 122, C.I. Pigment Violet 19 and C.I. Pigment Red 150. However, these magenta toners are low in printing density and may cause fog in some cases.

15 As described above, when a quinacridone pigment is used, light resistance is improved compared with the case where another pigment is used. However, such a pigment tends to lower the printing density of the resulting magenta toner. In order to raise the printing density 20 using the quinacridone pigment, it is necessary to use the pigment in a great amount. When the quinacridone pigment is used in a great amount, however, not only the cost of the resulting magenta toner is increased, but also the fixing ability of the toner is liable to lower.

25 [0004]

On the other hand, it is investigated to use a Naphthol AS pigment alone without using any quinacridone

pigment. Naphthol AS pigments are classified into a mono-azo system and a dis-azo system. However, mono-azo pigments are generally widely adopted.

Japanese Patent Application Laid-Open Nos. 2000-81734 and 2002-182433 disclose magenta toner particles comprising C.I. Pigment Red 31 as a mono-azo pigment in Examples thereof and are applied to a two-component development system. However, the investigation by the present inventors has revealed that when these toner is applied to formation of images by a non-magnetic one-component development system, not only the density of an image printed becomes low, but also hot offset occurs, and moreover storage stability becomes poor.

Japanese Patent Application Laid-Open No. 2002-72569 discloses a magenta toner comprising C.I. Pigment Red 150 as a mono-azo pigment. However, the investigation by the present inventors has revealed that not only this toner can form only images having a hue far from a hue by printing with inks, but also it is low in printing density and poor in low-temperature fixing ability and causes fog under high-temperature and high-humidity conditions.

[0005]

[Article 1] Japanese Patent Application Laid-Open No. 2002-156795

25 [Article 2] Japanese Patent Application Laid-Open No. 2000-81734

[Article 3] Japanese Patent Application Laid-Open No. 2002-

72569

[0006]

[Problems Sought for Solution by the Invention]

It is an object of the present invention to provide a
5 magenta toner which is high in printing density, causes no
fog and can reproduce a hue equivalent to printing with
inks.

Another object of the present invention is to provide
a magenta toner has low-temperature fixing ability and
10 causes no fog even under severe environments of low
temperature and low humidity, and high temperature and high
humidity.

A further object of the present invention is to
provide a magenta toner which prevents toner from breaking
15 in an image forming apparatus to low flowability, prevents
an image obtained by printing from fading and has little
possibility of causing an environmental problem even when a
transfer medium, on which an image has been formed with the
toner, is incinerated.

20 [0007]

[Means for solution of the Problems]

The present inventors have carried out an extensive
investigation with a view toward achieving these objects.
As a result, it has been found that the above-described
25 objects can be achieved by using specific pigments as a
magenta colorant in a magenta toner having magenta toner
particles comprising a binder resin and the magenta

colorant. The present invention has been led to completion on the basis of this finding.

According to the present invention, there is thus provided a magenta toner having magenta toner particles 5 comprising a binder resin and a magenta pigment, wherein the magenta colorant is a magenta pigment composed of a combination of C.I. Pigment Red 31 and C.I. Pigment Red 150.

[0008]

[Mode for Carrying out the Invention]

10 The details of the present invention are described below.

The magenta toner particles comprises a binder resin and a magenta pigment as essential components.

[0009]

15 As examples of the binder resin, may be mentioned resins heretofore widely used for toners, such as polystyrene, styrene-butyl acrylate copolymers, polyester resins and epoxy resins.

[0010]

20 The magenta pigment used in the present invention is composed of C.I. Pigment Red 31 and C.I. Pigment Red 150. The use of the magenta pigment composed of these two pigments can provide a magenta toner capable of forming images having a hue equivalent to magenta in printing with 25 inks. Since the magenta pigment contains no chlorine atom, there is little possibility that an environmental problem may be caused even when a transfer medium such as paper, on

which an image has been formed with the resulting magenta toner, is incinerated.

The surface of the magenta pigment used in the present invention may be treated with a rosin compound or 5 the like by publicly known method for the purpose of improving the dispersibility of the pigment in the magenta toner particles. However, if the amount of the treating agent to the magenta pigment is too great, the resulting magenta toner may cause fog under high-temperature and 10 high-humidity conditions in some cases. Accordingly, the amount of the treating agent used is preferably at most 20 parts by mass, more preferably at most 10 parts by mass, particularly preferably at most 5 parts by mass per 100 parts by mass of the magenta pigment.

15 **[0011]**

A proportion of C.I. Pigment Red 31 to C.I. Pigment Red 150 used is within the range of preferably from 30:70 to 80:20, more preferably from 40:60 to 70:30, particularly preferably from 50:50 to 60:40.

20 The amount of these magenta pigment is 1 to 10 parts by mass in total per 100 parts by mass of the binder resin.

[0012]

In the present invention, a charge control agent which is usually used is preferably contained in the 25 magenta toner particles for the purpose of controlling the charge level of the resulting magenta toner. Among charge control agents, charge control resins are particularly

preferred because they are high in compatibility with the binder resin and colorless and can provide a magenta toner stable in charging ability in the case of continuous high-speed color-printing. As the charge control resins, are 5 used quaternary ammonium (salt) group-containing copolymers prepared in accordance with a process described in Japanese Patent Application Laid-Open Nos. 63-60458, 3-175456, 3-243954 and 11-15192 and sulfonic (salt) group-containing copolymers prepared in accordance with a process described 10 in Japanese Patent Application Laid-Open Nos. 1-217464 and 3-15858.

A monomer unit having a quaternary ammonium (salt) group or sulfonic (salt) group contained in these copolymers is contained in a proportion of 0.5 to 15 % by 15 mass, preferably 1 to 10 % by mass in each copolymer. When the content of these monomer units falls within the above-described range, the charge level of the resulting toner is easy to be controlled, and the occurrence of fog can be lessened.

20 [0013]

The weight average molecular weight of the charge control resin is within the range of generally 2,000 to 50,000, preferably 4,000 to 40,000, more preferably 6,000 to 30,000. When the weight average molecular weight of the 25 charge control resin used falls within this range, the saturation and transparency of the resulting toner can be highly retained.

The glass transition temperature of the charge control resin is within the range of generally 40 to 80°C, preferably 45 to 75°C, more preferably 45 to 70°C. When the glass transition temperature of the charge control resin used falls within this range, a balance between storage stability and fixing ability in the resulting toner can be improved.

The proportion of the charge control resin used is within the range of generally 0.01 to 20 parts by mass, 10 preferably 0.1 to 10 parts by mass per 100 parts by mass of the binder resin.

[0014]

In the present invention, a parting agent is preferably contained in the magenta toner particles. 15 Examples of the parting agent include polyolefin waxes such as low molecular weight polyethylene, low molecular weight polypropylene and low molecular weight polybutylene; natural plant waxes such as candelilla, carnauba, rice, Japan wax and jojoba; petroleum waxes such as paraffin, 20 microcrystalline and petrolatum, and modified waxes thereof; synthetic waxes such as Fischer-Tropsch wax; and polyfunctional ester compounds such as pentaerythritol tetramyristate, pentaerythritol tetrapalmitate and dipentaerythritol hexamyristate.

25 These parting agents may be used either singly or in any combination thereof.

[0015]

Among these parting agents, synthetic waxes, terminal-modified polyolefin waxes, petroleum waxes and polyfunctional ester compounds are preferred. Among the polyfunctional ester compounds, pentaerythritol esters 5 whose endothermic peak temperatures upon heating fall within the range of 30 to 200°C, preferably 40 to 160°C, more preferably 50 to 120°C in a DSC curve as determined by a differential scanning calorimeter (DSC), and dipentaerythritol esters whose endothermic peak 10 temperatures fall within the range of 50 to 80°C are particularly preferred from the viewpoint of improving a balance between the fixing ability and the parting property in the resulting toner. Among the polyfunctional ester compounds such as pentaerythritol esters whose endothermic 15 peak temperatures upon heating fall within the range of 30 to 200°C, and dipentaerythritol esters whose endothermic peak temperatures fall within the range of 50 to 80°C, those having a molecular weight of at least 1,000, a solubility of 5 parts by mass in 100 parts by mass of 20 styrene at 25°C and an acid value of at most 10 mgKOH/g are particularly preferred because they exhibits a marked effect on lowering of the fixing temperature of the resulting magenta toner. The endothermic peak temperature is a value measured in accordance with ASTM D 3418-82. 25 Since the low-temperature fixing ability of the resulting toner is improved by using these parting agents, and a fixing region becomes broad (namely, offset margin becomes

great), this magenta toner can be applied to not only an image forming apparatus heretofore used, on a fixing roll of which an anti-offset liquid has been coated, but also an image forming apparatus that is not coated with such an 5 anti-offset liquid.

The proportion of the parting agent used is within the range of generally 0.5 to 50 parts by mass, preferably 1 to 20 parts by mass per 100 parts by mass of the binder resin.

10 [0016]

The magenta toner particles can be provided as particles of a so-called "core-shell type" (also called "capsule type") obtained by respectively using two different resin components for interiors (core layers) and 15 exteriors (shell layers) of particles in combination. In the particles of the core-shell type, the interiors (core layers) substance having a low softening point is coated with a substance having a softening point higher than the first-mentioned substance, whereby a balance between 20 lowering of fixing temperature and prevention of aggregation during storage can be improved.

The core layers of the core-shell type particles are generally formed by the binder resin, the magenta pigment, the charge control agent and the parting agent, and the 25 shell layer are formed by the binder resin alone.

[0017]

In the core-shell type particles, the volume average

particle diameter of the core particles is within the range of 3.0 to 12.0 μm , preferably 4.0 to 10.0 μm , more preferably 5.0 to 8.0 μm . The particle diameter distribution dv/dp represented by a ratio of the volume 5 average particle diameter dv to the number average particle diameter dp of the core particles is within the range of preferably 1.0 to 1.3, more preferably 1.0 to 1.2.

[0018]

No particular limitation is imposed on a mass ratio 10 of the core particles to the shell layers in the core-shell type particles. However, it is generally within the range of 80/20 to 99.9/0.1.

When the proportion of the shell layers is controlled within the above-described range, the resulting toner can 15 have good storage stability and low-temperature fixing ability in combination.

[0019]

The average thickness of the shell layers in the core-shell particles is within the range of generally 0.001 20 to 1.0 μm , preferably 0.003 to 0.5 μm , more preferably 0.005 to 0.2 μm . If the thickness of the shell layers is too great, the fixing ability of the magenta toner may possibly be deteriorated. If the thickness is too small to the contrary, the storage stability of the toner may 25 possibly be deteriorated. All the surfaces of the core particles forming the core-shell type toner particles are not necessarily coated with a shell layer, but a part of

the surfaces of the core particles may be coated with the shell layer.

The particle diameter of the core particles and the thickness of the shell layers in the core-shell type particles can be determined by directly measuring the size and shell thickness of each of particles selected at random from an electron photomicrograph thereof to calculate out respective average values when they can be observed through an electron microscope. If the core particle and the shell layer are difficult to be observed through the electron microscope, the thickness of the shell layers can be calculated out on the basis of the measured value of the particle diameter of the core particles and the amount of the shell-forming monomer used in the formation of the toner.

[0020]

The volume average particle diameter d_v of the magenta toner particles is within the range of 3.0 to 10.0 μm , preferably 4.0 to 9.0 μm , more preferably 5.0 to 8.0 μm . If the volume average particle diameter is too small, the flowability is lowered, and so its transferability may be lowered, blur may occur, or the printing density may be lowered. On the other hand, if this volume average particle diameter is too great, fog and flying-off of the resulting toner occur, and the resolution of an image formed with such a toner is deteriorated.

A particle diameter distribution d_v/dp that is a

ratio of the volume average particle diameter d_v to the number average particle diameter d_p is preferably within the range of 1.0 to 1.3, more preferably 1.0 to 1.2. If the particle diameter distribution is too great, the 5 resulting toner tends to cause blur or lower transferability, printing density and resolution.

The volume average particle diameter and particle diameter distribution of the magenta toner particles can be measured by means of, for example, a Multisizer 10 (manufactured by Beckmann Coulter Co.).

【0021】

In the magenta toner particles, an average spheroidicity r_l/r_s obtained by dividing a length r_l of each particle by its breadth r_s is within the range of 1.0 15 to 1.3, more preferably 1.0 to 1.2, particularly preferably 1.0 to 1.15. If the average spheroidicity is greater than 1.3, the transferability of the toner may be lowered in some cases.

The average spheroidicity can be easily controlled 20 within the above range by using a phase-inversion emulsification process, dissolution and suspension process, polymerization process or the like.

【0022】

The magenta toner according to the present invention 25 may be formed by the magenta toner particles alone. In order to improve cleaning ability, charging ability, flowability and storage stability of the resulting toner,

however, the toner is preferably containing an external additive. The external additive may be applied to the surfaces of the magenta toner particles by stirring these components in a mixer such as a Henschel mixer, or a part 5 thereof may be embedded therein.

Hexahedral inorganic fine particles are preferably used as the external additive. The hexahedral inorganic fine particles have a form of a hexahedron such as a cube or rectangular parallelopiped. They may be somewhat 10 deformed by, for example, rounding apexes thereof. A length ratio of the longest arris to the shortest arris among arrises making up the hexahedron is preferably within the range of 1 to 2, or is more preferably 1.

[0023]

15 No particular limitation is imposed on the chemical structure of the hexahedral inorganic fine particles.

However, calcium carbonate is mentioned as a representative thereof. No particular limitation is imposed on the volume average particle diameter of the 20 hexahedral inorganic fine particles. However, it is within the range of generally 0.05 to 10 μm . If this volume average particle diameter is too small, the cleaning ability of the resulting toner is lowered. If the volume average particle diameter is too great to the contrary, the 25 flowability of the toner is lowered, and so blur may occur, or image defects may be caused in some cases.

[0024]

The hexahedral inorganic fine particles are preferably subjected to a hydrophobicity-imparting treatment. As the hexahedral inorganic fine particles subjected to the hydrophobicity-imparting treatment, may be 5 used a commercially available product. However, they may be prepared by subjecting untreated inorganic fine particles to a hydrophobicity-imparting treatment with a silane coupling agent, silicone oil, fatty acid, fatty acid metal soap or the like.

10 [0025]

No particular limitation is imposed on the amount of the hexahedral inorganic fine particles used. However, it is within the range of preferably 0.05 to 5 parts by mass, more preferably 0.1 to 3 parts by mass per 100 parts by 15 mass of the magenta toner particles. If the amount used is too little, the effect of improving the cleaning ability becomes small. If the amount is too great to the contrary, the flowability of the resulting toner is lowered, and so blur may occur in some cases.

20 [0026]

Besides the hexahedral inorganic fine particles, fine particles, whose shape is spherical or indefinable, are preferably used as an external additive. As the fine particles whose shape is spherical or indefinable, any of 25 inorganic fine particles and organic fine particles may be used. However, inorganic fine particles are preferred from the viewpoint of controlling the flowability and charging

ability of the resulting toner. These fine particles may be used either singly or in any combination thereof.

[0027]

Examples of the inorganic fine particles, whose shape 5 is spherical or indefinable, include silica, titanium oxide, aluminum oxide, zinc oxide, tin oxide, barium titanate and strontium titanate. Among these, silica is preferred because fog upon printing can be lessened.

No particular limitation is imposed on the volume 10 average particle diameter of the inorganic fine particles. However, it is within the range of generally 5 to 500 nm, preferably 5 to 100 nm, more preferably 7 to 50 nm. If this volume average particle diameter is too small, the resulting toner undergoes charge-up at a low temperature 15 and a low humidity to lower its printing density. If the volume average particle diameter is too great to the contrary, the flowability of the resulting toner is lowered, and so blur may be liable to occur. The volume average particle diameter of the inorganic fine particles can be 20 measured by, for example, taking an electron microphotograph of the particles, and processing this photograph by means of an image processing analyzer [trade name "LUZEX IID", manufactured by NIRECO Corporation].

These inorganic fine particles preferably have a 25 hydrophobization degree of 30 to 90% as determined by a methanol method.

No particular limitation is imposed on the amount of

the inorganic fine particles. However, it is within the range of generally 0.1 to 5 parts by mass, preferably 0.3 to 3 parts by mass per 100 parts by mass of the magenta toner particles. If the amount added is too little, the 5 flowability of the resulting toner is lowered, and so blur may occur in some cases. If the amount is too great to the contrary, the flowability becomes too excessive, and so fog may occur in some cases.

[0028]

10 No particular limitation is imposed on the spherical or indefinable organic fine particles. From the viewpoint of inhibiting blocking between particles, however, it is desirable that the glass transition temperature or melting point of a compound forming such fine particles falls 15 within the range of preferably 80 to 250°C, more preferably 90 to 200°C.

Examples of the compound forming the organic fine particles include methyl methacrylate polymers and styrene-methyl methacrylate copolymers.

20 No particular limitation is imposed on the volume average particle diameter of the organic fine particles. However, it is within the range of generally 0.1 to 1 μm , preferably 0.1 to 0.8 μm . No particular limitation is imposed on the spheroidicity r_1/r_s of the organic fine 25 particles. However, it is within the range of generally 1.0 to 1.3, preferably 1.0 to 1.2. If this volume average particle diameter is too small, it may be impossible in

some cases to prevent the occurrence of toner filming. If the volume average particle diameter is too great to the contrary, the flowability of the resulting toner may be lowered in some cases. If the spheroidicity is too great, 5 the transferability of the resulting toner may be lowered in some cases.

No particular limitation is imposed on the amount of the organic fine particles added. However, it is within the range of generally 0.05 to 1 part by mass, preferably 10 0.1 to 0.5 part by mass per 100 parts by mass of the magenta toner particles. If the added amount is too little, a filming phenomenon tends to be occurred. If the amount is too great to the contrary, the flowability of the resulting toner becomes poor, and so blur may possibly be 15 liable to occur.

[0029]

No particular limitation is imposed on the production process of the magenta toner particles according to the present invention, and they can be produced by, for example, 20 (i) a grinding process, (ii) a polymerization process such as an emulsion polymerization process or suspension polymerization process, or (iii) a dissolution and suspension process. Among these production processes, the polymerization process is preferred in that toner, which 25 can meet the image quality of high resolution and the speeding-up of printing, are easily obtained.

Substantially spherical magenta-colored polymer particles

obtained by the suspension polymerization process among the polymerization processes are particularly preferred. The particles are made spherical, whereby the toner can be prevented from being broken in an image forming apparatus 5 to lower the flowability of the magenta toner.

[0030]

The production process of the magenta toner particles by the suspension polymerization process will hereinafter be described.

10 In the suspension polymerization process, a magenta pigment, a charge control agent, a parting agent and the like are dissolved or dispersed in a polymerizable monomer which is a low material of a binder resin to suspend in an aqueous dispersion medium containing a dispersion 15 stabilizer and a polymerization initiator is added thereto, then polymerization is initiated by heating the suspension to a prescribed temperature. After completing the polymerization, a remaining polymerizable monomer is distilled off, and the magenta-colored resin particles are 20 then collected by filtration, washing, dehydration and drying.

[0031]

In the present invention, it is preferred that the magenta pigment be mixed with the charge control resin in 25 advance to prepare a charge control resin composition. In this case, the magenta pigment is mixed in a proportion of generally 10 to 200 parts by mass, preferably 20 to 150

parts by mass per 100 parts by mass of the charge control resin.

An organic solvent is preferably used for the preparation of the charge control resin composition. The 5 use of the organic solvent makes the charge control resin soft and easy to mix with the magenta pigment. When no organic solvent is used, it is necessary to heat both components to such a temperature that the resin becomes soft to mix them. When an organic solvent is used, 10 especially, when the organic solvent has a low boiling point, the organic solvent may be evaporated in some cases by heating. It is thus preferable to mix both components at room temperature or while cooling them. Since a problem of odor may be caused in some cases when the organic 15 solvent remains in the resulting toner, the organic solvent is preferably removed in the course of the preparation of the charge control resin composition or the production of the toner. When no organic solvent is used, it is necessary to heat both components to such a temperature 20 that the resin becomes soft to mix them.

The amount of the organic solvent used is within the range of 0 to 100 parts by mass, preferably 5 to 80 parts by mass, more preferably 10 to 60 parts by mass per 100 parts by mass of the charge control resin. When the amount 25 of the organic solvent used falls within this range, a balance between dispersibility and processing ability becomes excellent. The whole amount of the organic solvent

may be added either at a time or in several portions while confirming a mixed state.

[0032]

When the organic solvent is used, it is preferable
5 that the solubility parameter (hereinafter referred to as
"SP value") thereof be within the range of 8 to 15
[cal/cm³]^{1/2}, and that the boiling point thereof be within
the range of 50 to 150°C. If the SP value of the organic
solvent is smaller than 8 [cal/cm³]^{1/2}, its polarity becomes
10 too low, and difficulty is encountered upon dissolution of
the charge control resin. If the SP value is greater than
15 [cal/cm³]^{1/2} to the contrary, the polarity becomes too
high, and difficulty is encountered upon dissolution of the
charge control resin. On the other hand, if the boiling
15 point of the organic solvent is lower than 50°C, the
organic solvent may be evaporated in some cases by heat
generated upon the mixing. If the boiling point is higher
than 150°C to the contrary, difficulty is liable to occur
upon removal of the organic solvent.

20 Specific examples of organic solvents (SP
value/boiling point) include methanol (14.5/65°C), ethanol
(10.0/78.3°C), propanol (11.9/97.2°C), diethyl ketone
(8.8/102°C), di-n-propyl ketone (8.0/144°C), di-isopropyl
ketone (8.0/124°C), methyl n-propyl ketone (8.3/102°C),
25 methyl isopropyl ketone (8.5/95°C), methyl n-butyl ketone
(8.5/127°C), methyl isobutyl ketone (8.4/117°C), toluene
(8.9/110°C), tetrahydrofuran (9.1/65°C), methyl ethyl

ketone (9.3/80°C), acetone (9.9/56°C) and cyclohexanone (9.9/156°C). These organic solvents may be used either singly or in any combination thereof. Among these, diethyl ketone, methyl n-propyl ketone, methyl n-butyl ketone, 5 methyl ethyl ketone/methanol mixed solvent, toluene/ethanol mixed solvent and toluene/propanol mixed solvent are preferred in view of solubility of the charge control resin and removal efficiency after the mixing.

[0033]

10 The mixing may be conducted by means of a mixer such as a roll mill, PLASTICODER (manufactured by Brabender Co.), LABOPLASTO MILL (manufactured by Toyo Seiki Co., Ltd.), kneader, single-screw extruder, twin-screw extruder, Banbury mixer or Buss Cokneader. When the organic solvent 15 is used, problems of odor and toxicity arise, and so a mixer capable of mixing in a closed system, in which the organic solvent does not leak, is preferably used.

20 A mixer equipped with a torque meter is preferred because dispersibility can be controlled by the level of torque.

The amount of the charge control resin composition is within the range of generally 2 to 20 parts by mass, preferably 3 to 15 parts by mass per 100 parts by mass of the polymerizable monomer for obtaining the after-mentioned 25 binder resin. If this amount used is too little, the charge control of the resulting toner is liable to become difficult. If the amount is too great to the contrary, the

resulting magenta toner undergoes moisture absorption, and so fog may occur in some cases.

[0034]

As examples of the polymerizable monomer for 5 obtaining the binder resin, may be mentioned monovinyl monomers, crosslinkable monomers and macromonomers. The polymerizable monomer is polymerized to provide a binder resin component.

Examples of the monovinyl monomers include aromatic 10 vinyl monomers such as styrene, vinyltoluene and α -methylstyrene; (meth)acrylic acid; derivatives of (meth)acrylic acid, such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, cyclohexyl (meth)acrylate, 15 isobonyl (meth)acrylate, dimethylaminoethyl (meth)acrylate and (meth)acrylamide; and monoolefin monomers such as ethylene, propylene and butylene.

The monovinyl monomers may be used either singly or in any combination thereof. Among these monovinyl monomers, 20 aromatic vinyl monomers, and combinations of an aromatic vinyl monomer and a derivative of (meth)acrylic acid are preferred.

[0035]

When a crosslinkable monomer and a crosslinkable 25 polymer are used together with the monovinyl monomer, hot offset can be effectively improved. The crosslinkable monomer is a monomer having at least 2 vinyl groups. As

specific examples thereof, may be mentioned aromatic divinyl compounds such as divinylbenzene, divinylnaphthalene and derivatives thereof; diethyl-type unsaturated carboxylic acid esters such as ethylene glycol 5 dimethacrylate and diethylene glycol dimethacrylate; compounds having 2 vinyl groups, such as N,N-divinylaniline and divinyl ether; and compounds having three or more vinyl groups, such as pentaerythritol triallyl ether and trimethylolpropane triacrylate. The crosslinkable polymer 10 is a polymer having two or more vinyl groups in the polymer. As specific examples thereof, may be mentioned esters obtained by subjecting a polymer, such as polyethylene, polypropylene, polyester or polypropylene glycol, having two or more hydroxyl groups in its molecule, and an 15 unsaturated carboxylic acid monomer such as acrylic acid or methacrylic acid to a condensation reaction. These crosslinkable monomers and crosslinkable polymers may be used either singly or in any combination thereof. The amount of these monomers and polymers used is within the 20 range of generally at most 10 parts by mass, preferably 0.1 to 2 parts by mass per 100 parts by mass of the monovinyl monomer.

[0036]

It is preferable to use a macromonomer together with 25 the monovinyl monomer because a balance between the storage stability and low-temperature fixing ability of the resulting toner is improved. The macromonomer is an

oligomer or polymer having a polymerizable carbon-carbon unsaturated double bond at its molecular chain terminal and a number average molecular weight generally ranging from 1,000 to 30,000. When the number average molecular weight 5 falls within the above-described range, the fixing ability and storage stability of the resulting toner can be retained without impairing the melt properties of the macromonomer. It is hence preferable that the number average molecular weight be within the above range.

10 Examples of groups having the polymerizable carbon-carbon unsaturated double bond located at its molecular chain terminal include acryloyl and methacryloyl groups. Among these, the methacryloyl group is preferred from the viewpoint of easiness of copolymerization.

15 [0037]

The macromonomer is preferably that giving a polymer having a glass transition temperature higher than that of a polymer obtained by polymerizing the monovinyl monomer.

As examples of the macromonomer used in the present 20 invention, may be mentioned polymers obtained by polymerizing styrene, styrene derivatives, methacrylic esters, acrylic esters, acrylonitrile and methacrylonitrile either singly or in combination of two or more monomers thereof, and macromonomers having a polysiloxane skeleton. 25 Among these, hydrophilic macromonomers, in particular, polymers obtained by polymerizing methacrylic esters or acrylic esters either singly or in combination of two or

more monomers thereof are preferred.

When the macromonomer is used, the amount of the macromonomer used is within the range of generally 0.01 to 10 parts by mass, preferably 0.03 to 5 parts by mass, more 5 preferably 0.05 to 1 part by weight per 100 parts by weight of the monovinyl monomer. The macromonomer is preferably used in the amount within the above-described range because the storage stability of the resulting toner can be retained without deteriorating the fixing ability thereof.

10 [0038]

As examples of the dispersion stabilizers, may be mentioned metallic compounds, such as sulfates such as barium sulfate and calcium sulfate; carbonates such as barium carbonate, calcium carbonate and magnesium 15 carbonate; phosphates such as calcium phosphate; and metal oxides such as aluminum oxide and titanium oxide; and besides, metal hydroxides such as aluminum hydroxide, magnesium hydroxide and ferric hydroxide; water-soluble polymers such as polyvinyl alcohol, methyl cellulose and 20 gelatin; and surfactants such as anionic surfactants, nonionic surfactants and amphoteric surfactants. These dispersion stabilizers may be used either singly or in any combination thereof.

Among these dispersion stabilizers, colloid of a 25 metallic compound, particularly, a hardly water-soluble metal hydroxide is preferred because the particle diameter distribution of the colored polymer particles to be formed

can be narrowed, and remaining tendency of the dispersion stabilizer after washing is little, and an image can be brightly or sharply reproduced.

[0039]

5 The colloid of the hardly water-soluble metal hydroxide preferably has a particle diameter distribution that a particle diameter D_{50} that the cumulative particle number counting from a smaller particle diameter side is 50% is at most 0.5 μm , and a particle diameter D_{90} that the 10 cumulative particle number is 90% is at most 1 μm . If the particle diameter of the colloid is too great, the stability of the polymerization is broken, and the storage stability of the resulting toner is deteriorated.

[0040]

15 The dispersion stabilizer is used in a proportion of generally 0.1 to 20 parts by mass per 100 parts by mass of the polymerizable monomer. The dispersion stabilizer is preferably used in the proportion falling within the above-described range because sufficient polymerization stability 20 is achieved, formation of polymer aggregates is inhibited, and colored polymer particles having a desired particle diameter can be obtained.

[0041]

As examples of the polymerization initiator, may be 25 mentioned persulfates such as potassium persulfate and ammonium persulfate; azo compounds such as 4,4'-azobis-(4-cyanovaleric acid), 2,2'-azobis(2-methyl-N-(2-

hydroxyethyl)propionamide, 2,2'-azobis(2-amidinopropane) dihydrochloride, 2,2'-azobis(2,4-dimethylvaleronitrile) and 2,2'-azobisisobutyronitrile; and peroxides such as di-t-butyl peroxide, dicumyl peroxide, lauroyl peroxide, benzoyl 5 peroxide, t-butyl peroxy-2-ethylhexanoate, t-hexyl peroxy-2-ethylhexanoate, t-butyl peroxy-pivalate, di-isopropyl peroxydicarbonate, di-t-butyl peroxyisophthalate, 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate and t-butyl peroxyisobutyrate. Redox initiators composed of 10 combinations of these polymerization initiators with a reducing agent may also be used.

[0042]

It is preferable to select an oil-soluble polymerization initiator soluble in the used polymerizable 15 monomer from among these. A water-soluble polymerization initiator may also be used in combination with the above-described initiator as needed. The polymerization initiator is used in a proportion of generally 0. 1 to 20 parts by mass, preferably 0.3 to 15 parts by mass, more 20 preferably 0.5 to 10 parts by mass per 100 parts by weight of the polymerizable monomer.

The polymerization initiator may be added into the polymerizable monomer composition in advance. In order to prevent premature polymerization in, for example, the step 25 of preparing the polymerizable monomer composition or the step of forming the droplets, however, the polymerization initiator may be directly added into a suspension after

completion of the formation of the droplets in the case of suspension polymerization, or an emulsion after completion of a emulsifying step in the case of emulsion polymerization.

5 [0043]

Upon the polymerization, a molecular weight modifier is preferably used. As examples of the molecular weight modifier, may be mentioned mercaptans such as t-dodecylmercaptan, n-dodecylmercaptan, n-octylmercaptan and 10 2,2,4,6,6-pentamethylheptane-4-thiol; and halogenated hydrocarbons such as carbon tetrachloride and carbon tetrabromide. These molecular weight modifiers may be added before the initiation of the polymerization or in the course of the polymerization. The molecular weight 15 modifier is used in a proportion of generally 0.01 to 10 parts by mass, preferably 0.1 to 5 parts by mass per 100 parts by weight of the polymerizable monomer.

[0044]

Examples of a process for producing the magenta toner 20 particles having the core-shell structure include processes such as a spray drying process, interfacial reaction process, *in-situ* polymerization process and phase separation process. More specifically, magenta toner particles obtained by a grinding process, polymerization 25 process, association process, phase-inversion emulsification process or the like are used as core particles, a shell layer is formed on the core particles,

whereby the magenta toner particles having the core-shell structure can be obtained. Among these production processes, *in-situ* polymerization process and phase-inversion emulsification process are preferred from the 5 viewpoint of production efficiency.

[0045]

The production process of the magenta toner particles having the core-shell structure by the *in-situ* polymerization process will hereinafter be described.

10 A polymerizable monomer (polymerizable monomer for shell) for forming shell layers and a polymerization initiator are added into an aqueous dispersion medium with core particles dispersed therein to conduct polymerization, whereby magenta toner particles of the core-shell structure 15 can be obtained.

As specific processes for forming the shell layers, may be mentioned a process, in which a polymerizable monomer for shell is added into a reaction system of a polymerization reaction conducted for obtaining core 20 particles, and the polymerization reaction is continued; a step-wise process, in which core particles obtained in a separate reaction system are charged into an aqueous dispersion medium, and a polymerizable monomer for shell is added to the resultant dispersion to conduct polymerization, 25 and the like.

The polymerizable monomer for shell may be added into the reaction system at a time, or may be added continuously

or intermittently by means of a pump such as a plunger pump.

[0046]

As the polymerizable monomer for shell, monomers respectively forming polymers having a glass transition 5 temperature exceeding 80°C, such as styrene, acrylonitrile and methyl methacrylate, are preferably used either singly or in combination of two or more monomers thereof.

[0047]

A water-soluble polymerization initiator is 10 preferably added upon the addition of the polymerizable monomer for shell because the magenta toner particles of the core-shell structure are easy to be obtained. It is considered that when the water-soluble polymerization initiator is added upon the addition of the polymerizable 15 monomer for shell, the water-soluble polymerization initiator enters in the vicinity of each surface of the core particles to which the polymerizable monomer for shell has migrated, and consequently a polymer (shell) layer is easy to be formed on each surface of the core particles.

[0048]

As examples of the water-soluble polymerization initiator, may be mentioned persulfates such as potassium persulfate and ammonium persulfate; and azo type initiators such as 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)- 25 propionamide] and 2,2'-azobis-[2-methyl-N-[1,1-bis(hydroxymethyl)ethyl]propionamide. The amount of the water-soluble polymerization initiator used is within the

range of generally 0.1 to 50 parts by mass, preferably 1 to 30 parts by mass per 100 parts by mass of the polymerizable monomer for shell.

[0049]

5 **[Examples]**

The present invention will hereinafter be described more specifically by the following examples and comparative examples. However, the present invention is not limited to these examples alone. All designations of "part" or 10 "parts" and "%" mean part or parts by mass and % by mass unless expressly noted.

Various physical properties and characteristics in the present invention were evaluated in accordance with the following respective methods.

15 **[0050]**

1. Physical properties of magenta toner

(1) Average particle diameter and particle diameter distribution of magenta toner particles:

The volume average particle diameter d_v and particle 20 diameter distribution, i.e., a ratio d_v/d_p of the volume average particle diameter to the number average particle diameter d_p , of magenta toner particles were measured by means of a MULTISIZER (manufactured by Beckmann Coulter Co.). The measurement by this Multisizer was conducted 25 under the following conditions:

aperture diameter: 100 μm ;

medium: Isothone II, concentration: 10%; and

the number of particles measured: 100,000 particles.

(2) Spheroidicity:

A photograph of toner particles was taken by a scanning electron microscope, and the photograph was read 5 in an image processor, into which a Nexus 9000 type software had been incorporated, to determine a value r_1/r_s by dividing a length r_1 of each toner particle by a breadth r_s thereof. The number of particles measured was 100 particles, and an average value of the measured values was 10 regarded as an average spheroidicity.

[0051]

(3) Charge level:

A charge level was measured under respective environments of L/L environment of 10°C in temperature and 15 20% in humidity, N/N environment of 23°C in temperature and 50% in humidity, and H/H environment of 35°C in temperature and 80% in humidity.

More specifically, a printer on the market (manufactured by Oki Data Corporation, trade name 20 "MICROLINE 3010C") of the non-magnetic one-component development system was charged with a toner sample and left to stand for a day under the respective environments described above, and a half-tone print pattern was then printed by 5 sheets. Thereafter, the toner on a 25 development roller was sucked by a suction type charge level meter to measure a charge level per unit mass from a charge level of the toner sucked and an amount of the toner

sucked.

(4) Storage stability:

About 20 g of a toner sample were precisely weighed (W1) and placed in a closed bottle. The bottle was sunk 5 into a constant-temperature water bath controlled to 55°C. The bottle was taken out of the water bath after 8 hours had elapsed, and the toner contained in the bottle was transferred to a 42-mesh sieve so as not to destroy the structure of the toner as much as possible. The sieve was 10 vibrated for 30 seconds by means of a powder-measuring device ("POWDER TESTER", trade name; manufactured by Hosokawa Micron Corporation) with vibration intensity preset to 4.5. The weight of the toner remaining on the sieve was then measured to regard it as the weight (W2) of 15 the toner aggregated. A percentage (% by weight) of the weight W2 of the aggregated toner to the weight W1 of the toner sample was calculated out. The value was used as an index to the storage stability of the toner sample. The smaller the value, the higher the storage stability.

20 [0052]

2. Evaluation of image quality:

(1) Color tone:

After paper for printing was set in the above-described printer, a toner sample was charged into a 25 developing device, and the printer was left to stand for a day under (N/N) environment of 23°C in temperature and 50% in humidity, solid printing was conducted. With respect to

the paper, on which the solid printing had been conducted, the $L^*a^*b^*$ color space thereof was measured by means of a spectroscopic color-difference meter (manufactured by Nippon Denshoku K.K., model name "SE2000"). With respect to a hue difference from the magenta of Japan Color, a color tone of Japan Color Standard Paper measured likewise and a color tone obtained by printing with the toner sample are represented as coordinates of the $L^*C^*H^*$ color space to calculate out the hue difference ΔH in accordance with the following equation:

$$\Delta H^* = [(\Delta E^*)^2 - (\Delta L^*)^2 - (\Delta C^*)^2]^{1/2}$$

wherein ΔE^* : a color difference by the $L^*a^*b^*$ color space,

ΔL^* : a lightness index difference between 2 object colors in the $L^*a^*b^*$ color space, and

ΔC^* : a difference between 2 object colors, ab chromas in the $L^*a^*b^*$ color space.

The amount of the toner attached to the surface of the paper in the solid printing was controlled so as to be about 0.45 mg/cm^2 .

20 (2) Printing density:

After paper for printing was set in the above-described printer, a toner sample was charged into a developing device, and the printer was left to stand for a day under H/H environment of 35°C in temperature and 80% in humidity, printing was continuously conducted from the beginning at a density of 5%, and solid printing was conducted upon printing on the 20,000-th paper sheet. With

respect to the solid-printed paper sheet, the printing density was measured by means of a color reflection densitometer (manufactured by X-Light Co., model name "404A").

5 [0053]

(3) Fog:

Using the above-described printer, the printer was left to stand for a day under each environment of L/L environment of 10°C in temperature and 20% in humidity, N/N 10 environment of 23°C in temperature and 50% in humidity and H/H environment of 35°C in temperature and 80% in humidity, printing was continuously conducted at a density of 5%. After conducting printing on 20,000 sheets of paper, blank printing of a sheet of paper was conducted, the blank 15 printing was stopped on the way, and a toner in an unprinted area on a photosensitive member after development was taken out using a pressure-sensitive adhesive tape (product of Sumitomo 3M Limited, trade name "SCOTCH MENDING TAPE 810-3-18"). This adhesive tape was applied to new 20 paper for printing. The color tone B of the paper for printing, to which this adhesive tape had been applied, was measured by the spectroscopic color-difference meter, and the color tone A of paper for printing, to which only a pressure-sensitive adhesive tape had been applied, was 25 measures likewise. Their color tones were represented as coordinates of the L*a*b* color space to calculate out a color difference ΔE^* to regard it as a fog value. The

smaller the value, the less the fog.

[0054]

(4) Fixing temperature:

The above-described printer was modified in such a
5 manner that the temperature of a fixing roll can be varied.
This modified printer was used to vary the temperature of
the fixing roll at intervals of 5°C and measuring the
fixing rate of a toner sample at each temperature, thereby
conduct the fixing test of determine the relationship
10 between temperature and fixing rate.

In order to stabilize the temperature of the fixing
roll varied, the modified printer was left to stand for at
least 5 minutes at each temperature set, and solid printing
was then conducted on paper for printing by the modified
15 printer. With respect to the solid-printed area of the
paper printed, the fixing rate was calculated from a ratio
of printing densities before and after a peeling operation
using a tape. More specifically, assuming that the image
density before the peeling of the tape is ID_{before} , and the
20 image density after the peeling of the tape is ID_{after} , the
fixing rate is calculated out in accordance with the
following equation:

$$\text{Fixing rate (\%)} = (ID_{after}/ID_{before}) \times 100$$

The peeling operation of the tape is a series of
25 operation that a pressure-sensitive adhesive tape (product
of Sumitomo 3M Limited, trade name "SCOTCH MENDING TAPE
810-3-18") is applied to a measuring area of paper for test

to cause the tape to adhere to the paper by pressing the tape under a fixed pressure, and the adhesive tape is then peeled at a constant rate in a direction along the paper.

In this fixing test, a temperature of the fixing roll, 5 at which a fixing rate of the toner amounted to 80%, was defined as a fixing temperature of the toner.

(5) Hot offset temperature:

The temperature of the fixing roll was varied in the same manner as in the measurement of the fixing temperature 10 to conduct solid printing, thereby measuring a temperature, at which hot offset occurred. The temperature of the fixing roll, at which hot offset occurred, was defined as a hot offset temperature of the toner.

[0055]

15 [Example 1]

In 100 parts of a charge control resin (weight average molecular weight: 18,000; glass transition temperature: 67°C) obtained by polymerizing a monomer mixture composed of 82% of styrene, 11% of n-butyl acrylate 20 and 7% of 2-acrylamido-2-methylpropanesulfonic acid, were dispersed 24 parts of methyl ethyl ketone and 6 parts of methanol, and the dispersion was kneaded by rolls while cooling it. At the time the charge control resin wound around the rolls, 55 parts of C.I. Pigment Red 31 and 45 25 parts of C.I. Pigment Red 150 were gradually added as a magenta pigment, and the resultant mixture was kneaded for 1 hour to prepare a charge control resin composition. At

this time, a nip between the rolls was preset to 1 mm at the beginning of the kneading, gradually widened after this and finally widened to 3 mm. An organic solvent (4/1 mixed solvent of methyl ethyl ketone/methanol) was additionally 5 added several times according to the kneaded state of the charge control resin.

A part of the charge control resin composition was taken out, and toluene was added to this part to dissolve it, thereby preparing a 5% toluene solution of the charge 10 control resin composition. A doctor blade at an interval of 30 μm was used to apply the mix solution on to a glass plate and dried to form a sheet. This sheet was observed through a optical microscope. As a result, no magenta pigment particle having a length of 0.2 μm or greater was 15 present in a visual field 100 μm square.

[0056]

An aqueous solution with 6.9 parts of sodium hydroxide (alkali metal hydroxide) dissolved in 50 parts of ion-exchanged water was gradually added to an aqueous 20 solution with 9.8 parts of magnesium chloride (water-soluble polyvalent metal salt) dissolved in 250 parts of ion-exchanged water under stirring to prepare a dispersion of magnesium hydroxide colloid (colloid of hardly water-soluble metal hydroxide). The particle diameter 25 distribution of the colloid prepared was measured. As a result, the particle diameter was 0.38 μm in terms of D_{50} (50% cumulative value of number particle diameter

distribution) and 0.82 μm in terms of D_{90} (90% cumulative value of number particle diameter distribution).

[0057]

A polymerizable monomer for core composed of 80.5 parts of styrene, 19.5 parts of n-butyl acrylate, 0.5 parts of divinylbenzene and 0.25 parts of a polymethacrylic ester macromonomer (product of Toagosei Chemical Industry Co., Ltd., trade name "AA6") were mixed under stirring with 12 parts of the above-described charge control resin 10 composition, 2 parts of TDM and 10 parts of dipentaerythritol hexamyrystate into a uniform dispersion, thereby obtaining a polymerizable monomer composition for core.

One part of methyl methacrylate and 100 parts of 15 water were subjected to a finely dispersing treatment by an ultrasonic emulsifier to obtain an aqueous dispersion of a polymerizable monomer for shell. The diameter of droplets of the polymerizable monomer for shell was measured by means of (SALD2000A Model, manufactured by Shimadzu 20 Corporation) and found to be 1.6 μm in terms of D_{90} .

[0058]

After the polymerizable monomer composition for core was poured into the colloidal dispersion of magnesium hydroxide obtained in the above step, and the mixture was stirred 25 until droplets became stable, 6 parts of t-butyl peroxy-2-ethylhexanoate (product of Nippon Oil & Fats Co., Ltd., trade name "PERBUTYL O") were added. Thereafter, the

resultant dispersion was stirred 30 minutes at 15,000 rpm under high shearing force by means of a EBARA MILDER to form finer droplets of the polymerizable monomer composition. A reactor equipped with an agitating blade 5 was charged with the aqueous dispersion of the polymerizable monomer composition for core to initiate a polymerization reaction at 90°C. At the time a conversion into a polymer reached almost 100%, the reaction mixture was sampled to measure a volume average particle diameter 10 of core particles. As a result, it was 7.4 μm . The above aqueous dispersion of the polymerizable monomer for shell and 0.2 parts of 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (product of Wako Pure Chemical Industries, Ltd., trade name "VA-086") dissolved in 65 15 parts of distilled water were charged into the reactor, and the polymerization was then continued for 8 hours. After the temperature of the aqueous dispersion was lowered to 80°C while retaining agitation, and N_2 was introduced while retaining this temperature to distil off polymerizable 20 monomer residues, the residue was cooled to obtain an aqueous dispersion of magenta toner particles at pH 9.5.

[0059]

The pH of the system was adjusted to 5 or lower with sulfuric acid while stirring the aqueous dispersion of the 25 above magenta toner particles to conduct acid washing (25°C, 10 minutes). After water was then separated by filtration, 500 parts of ion-exchanged water were newly added to form a

slurry again, and the slurry was washed with water.

Thereafter, the dehydration and water washing were repeated several times, and solids were then separated by filtration.

The solids were dried at 45°C for 2 days by a dryer to

5 obtain magenta toner particles.

[0060]

The volume average particle diameter d_v of the dry magenta toner particles was 7.4 μm , a particle diameter distribution d_v/d_p was 1.23, and r_l/r_s was 1.1.

10 Into 100 parts of the magenta toner particles obtained above were mixed 0.3 parts of cubical calcium carbonate (product of Maruo Calcium Co., Ltd., trade name "CUBE-03BHS") having a volume average particle diameter of 0.3 μm , 0.5 parts of indefinable finely particulate silica 15 (product of Nippon Aerosil Co., Ltd., trade name "RX-300") subjected to a hydrophobicity-imparting treatment and 2.0 parts of indefinable finely particulate silica (product of Nippon Aerosil Co., Ltd., trade name "RX-50") subjected to a hydrophobicity-imparting treatment, by means of a 20 Henschel mixer to prepare a magenta toner.

The properties of the toner thus obtained and the results of the evaluation as to image quality are shown in Table 1.

[0061]

25 [Comparative Example 1]

A 2-liter 4-necked flask equipped with a high-speed agitating machine, TK type homomixer (manufactured by

Tokushu Kika Kogyo Co., Ltd.) was charged with 360 parts of ion-exchanged water and 430 parts of a 0.1 mol/liter aqueous solution of Na_3PO_4 . The rotating speed of the high-speed agitating machine was preset to 12,000 rpm, and the 5 system was heated to 65°C. To this aqueous solution, were added 34 parts of a 1.0 mol/liter aqueous solution of CaCl_2 to prepare an aqueous dispersion with a hardly water-soluble dispersion stabilizer $\text{Ca}_3(\text{PO}_4)_2$ finely dispersed therein.

10 [0062]

On the other hand, a mixture composed of 43 parts of styrene, 4.5 parts of C.I. Pigment Red 122 (content of calcium abietate: 0.5 parts) treated with calcium abietate, 2.3 parts of C.I. Pigment Red 150 (content of calcium 15 abietate: 0.3 parts) treated with calcium abietate, 3 parts of a charge control agent (product of Orient Chemical Industries Ltd., trade name "E-89") and 6 parts of a polyester resin (peak molecular weight = 5,000, acid value = 20 mg KOH/g) was dispersed for 3 hours by means of an 20 ATTRITOR (manufactured by Mitsui Kinzoku Kogyo Co., Ltd.) to prepare a pigment-dispersed composition.

[0063]

The whole amount (58.8 parts) of the above pigment-dispersed composition was added to a mixture of 40 parts of 25 styrene, 17 parts of n-butyl acrylate, 0.2 parts of divinylbenzene and 15 parts of a wax component (higher alcohol wax, melting point = 70°C) in an container, the

contents were dispersed and dissolved while being heated to 70°C, and 3 parts of 2,2'-azobis(2,4-dimethylvaleronitrile) were added to prepare a polymerizable monomer composition as a dispersoid.

5 [0064]

The polymerizable monomer composition was poured into the above aqueous dispersion medium, and the resultant mixture was stirred for 5 minutes while retaining the rotating speed of a high-speed agitating machine at 15,000 rpm under N₂ atmosphere at an internal temperature of 65°C to form droplets of the polymerizable monomer composition. After the step of forming the droplets, the agitating machine was changed to that equipped with a paddle-agitating blade to conduct polymerization with the temperature kept at the same temperature while stirring at 200 rpm, and the polymerization reaction was completed at the time a conversion of the polymerizable monomer into a polymer reached almost 100%.

After completion of the polymerization, remained polymerizable monomers were distilled off heating under reduced pressure. After cooling, dilute hydrochloric acid was added to the reaction mixture to dissolve the hardly water-soluble dispersing agent. After washing with water was conducted several times repeatedly, a drying treatment was conducted to obtain magenta toner particles.

[0065]

Into 100 parts of the magenta toner particles

obtained above were mixed 1.5 parts of indefinable finely particulate silica (product of Nippon Aerosil Co., Ltd., trade name "R-202") subjected to a hydrophobicity-imparting treatment, by means of a Henschel mixer to prepare a 5 magenta toner.

The properties of the magenta toner thus obtained and the results of the evaluation as to image quality are shown in Table 1.

[0066]

10 [Comparative Example 2]

A 2-liter 4-necked flask equipped with a high-speed agitating machine, TK type homomixer (manufactured by Tokushu Kika Kogyo Co., Ltd.) was charged with 360 parts of ion-exchanged water and 430 parts of a 0.1 mol/liter 15 aqueous solution of Na_3PO_4 . The rotating speed of the high-speed agitating machine was preset to 12,000 rpm, and the system was heated to 65°C. To this aqueous solution, were added 34 parts of a 1.0 mol/liter aqueous solution of CaCl_2 to prepare an aqueous dispersion containing a fine hardly 20 water-soluble dispersion stabilizer $\text{Ca}_3(\text{PO}_4)_2$.

[0067]

On the other hand, as a dispersoid, after a mixture composed of 83 parts of styrene, 17 parts of n-butyl acrylate, 6.6 parts of C.I. Pigment Red 150 (content of 25 calcium abietate: 0.6 parts) treated with calcium abietate, 5 parts of a polyester resin ($M_w = 25,000$), 0.03 parts of d-t-butylsalicylic acid and 15 parts of an ester wax ($M_n =$

1,000, $M_w/M_n = 1.9$) was dispersed for 3 hours by means of ATTRITOR manufactured by Mitsui Kinzoku Kogyo Co., Ltd., 3 parts of 2,2'-azobis(2,4-dimethylvaleronitrile) were added to prepare a polymerizable monomer composition.

5 [0068]

The polymerizable monomer composition was poured into the above aqueous dispersion medium, and the resultant mixture was stirred for 5 minutes while retaining the rotating speed of a high-speed agitating machine at 15,000 10 rpm under N_2 atmosphere at an internal temperature of $60^\circ C$ to form droplets of the polymerizable monomer composition. Thereafter, the agitating machine was changed to that equipped with a paddle-agitating blade to conduct polymerization for 5 hours with the temperature kept at the 15 same temperature while stirring at 200 rpm.

After completion of the polymerization, sodium hydrogencarbonate was added into the aqueous dispersion medium to adjust the pH to 11 again, 1 part of potassium persulfate that is a water-soluble initiator was 20 additionally added to conduct distillation for 5 hours under a reduced pressure of 350 mmHg at an internal temperature of $80^\circ C$. After cooling, dilute hydrochloric acid was added to adjust the pH of the aqueous dispersion medium to 1.2, thereby dissolving the hardly water-soluble 25 dispersing agent. After filtration and washing with water were conducted several times repeatedly, and solid-liquid separation was performed, the resultant solids were

subjected to a drying treatment to obtain magenta toner particles.

15 [0069]

Into 100 parts of the magenta toner particles obtained above were added 0.7 parts of titanium oxide subjected to a hydrophobicity-imparting treatment and having an average particle diameter of 30 nm and 0.7 parts of finely particulate silica (product of Nippon Aerosil Co., Ltd., trade name "R-202") subjected to a hydrophobicity-imparting treatment, and these components were mixed by means of a Henschel mixer to prepare a magenta toner.

The properties of the magenta toner thus obtained and the results of the evaluation as to image quality are shown in Table 1.

20 15 [0070]

[Comparative Example 3]

After 100 parts of a polyester resin (condensation polymer of propoxylated bisphenol A and fumaric acid, acid value: 10.8 mg KOH/g), 4 parts of a charge control agent (aluminum compound of di-t-butylsalicylic acid) having negatively charging ability and 5 parts of C.I. Pigment Red 31 were sufficiently premixed by means of a Henschel mixer, the resultant mixture was melt-kneaded by a twin-screw extruder. After cooling the kneaded product, it was 25 coarsely ground to the size of about 1 to 2 mm by means of a hammer mill, and the resultant coarse particles were finely ground by an air-jet type mill. Finely ground

powder and coarsely ground powder were simultaneously precisely removed from the finely ground product by a multi-division classifier, thereby obtaining magenta toner particles having an average particle diameter of 8.0 μm .

5 [0071]

Into 100 parts of the magenta toner particles obtained above were mixed 1.5 parts of finely particulate silica (product of Nippon Aerosil Co., Ltd., trade name "R-202") subjected to a hydrophobicity-imparting treatment by 10 means of a Henschel mixer to prepare a magenta toner.

The properties of the magenta toner thus obtained and the results of the evaluation as to image quality are shown in Table 1.

[0072]

[Table 1]

	Japan Color Magenta	Ex.	Comp. Ex.		
		1	1	2	3
Magenta pigment		PR31 PR150	PR122 PR150	PR150	PR31
Properties of toner particles					
Volume average particle diameter (μm)		7.2	8.2	7.8	8.0
Particle diameter distribution		1.23	1.39	1.42	1.47
Average spheroidicity		1.13	1.20	1.22	1.53
Charge level ($\mu\text{C/g}$)					
L/L environment		-42	-60	-30	-35
N/N environment		-32	-55	-25	-25
H/H environment		-35	-18	-14	-20
Storage stability (%)		2.0	3.5	4.5	50
Evaluation of image quality					
Hue					
L*	44.26	43.92	51.17	49.20	48.72
a*	69.06	66.49	64.56	59.83	57.43
b*	-9.37	-5.65	-16.49	4.21	-1.73
Hue difference (ΔH)		3.24	7.85	13.23	6.62
Amount attached on to paper (mg/cm^2)		0.45	0.45	0.46	0.44
Printing density		1.49	1.34	1.39	1.31
Fog					
L/L environment		0.3	1.5	0.7	0.4
N/N environment		0.1	1.1	1.5	1.2
H/H environment		0.7	2.4	6.2	1.1
Fixing temperature ($^{\circ}\text{C}$)		140	170	170	140
Hot offset temperature ($^{\circ}\text{C}$)		200	200	200	150

(Note)

PR31: C.I. Pigment Red 31

PR122: C.I. Pigment Red 122

5 PR150: C.I. Pigment Red 150

[0073]

From the results shown in Table 1, the following

facts are known.

It is known that the magenta toner of Comparative Example 1 making use of C.I. Pigment Red 122 and C.I.

Pigment Red 150 which are different from the magenta

5 pigment specified by the present invention is much removed in hue from the magenta of the Japan Color standard paper printed by inks, low in printing density, liable to cause fog under the respective environments and also poor in low-temperature fixing ability.

10 It is known that the magenta toner of Comparative Example 2 making use of C.I. Pigment Red 150, which is different from the magenta pigment specified by the present invention, alone as a magenta pigment is much removed in hue from the magenta of the Japan Color standard paper 15 printed by inks, low in printing density, liable to cause fog under both N/N environment and H/H environment and also poor in low-temperature fixing ability.

It is known that the magenta toner of Comparative Example 3 making use of C.I. Pigment Red 31, which is 20 different from the magenta pigment specified by the present invention, alone as a magenta pigment is much removed in hue from the magenta of the Japan Color standard paper printed by inks, low in printing density, liable to cause fog under both N/N environment and H/H environment, easy to 25 cause hot offset and also poor in storage stability of the toner.

On the other hand, the magenta toner of Example 1

according to the present invention can form an image of a hue near to the magenta of the Japan Color standard paper printed by inks and is high in printing density, hard to cause fog, excellent in low-temperature fixing ability and 5 hard to cause hot offset even after conducting printing of 20,000 sheets as a durability test or even under any environment.

[0074]

[Effects of the Invention]

10 The magenta toners according to the present invention are high in printing density, cause no fog and can reproduce a magenta hue equivalent to printing with inks. The magenta toners according to the present invention can fix at a low temperature, and are hard to cause fog even 15 under severe environments of low temperature and low humidity, and high temperature and high humidity. Further, the magenta toners according to the present invention prevent their magenta toner particles from breaking in an image forming apparatus to low flowability, prevents images 20 obtained by printing from fading and have little possibility of causing an environmental problem even when transfer media, on which images have been formed with the toners, are incinerated.

[Document Name] Abstract

[Abstract]

[Object] To provide a magenta toner which is high in printing density, causes no fog and can reproduce a magenta hue equivalent to printing with inks. To provide a magenta toner which can fix at a low temperature, and is hard to cause fog even under severe environments of low temperature and low humidity, and high temperature and high humidity.

5 Further, to provide a magenta toner which prevents breaking in an image forming apparatus to low flowability, prevents images obtained by printing from fading and have little 10 possibility of causing an environmental problem even when transfer media, on which images have been formed with the toners, are incinerated.

15 [Constitution] A magenta toner having a magenta toner particles comprising a binder resin and a magenta pigment, wherein the magenta pigment is composed of C.I. Pigment Red 31 and C.I. Pigment Red 150.

[Selected Figure of Drawings] None.